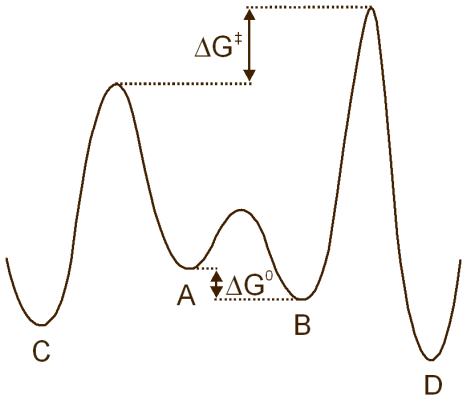
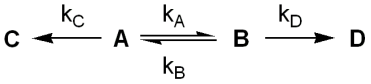
The Curtin-Hammett-Principle



A kinetic concept for systems like:



mostly A and B are conformational isomers

Curtin-Hammett-conditions:
- k_A, k_B >> k_C, k_D (>10 times larger)
- k_A, k_B of the same order of magnitude

it follows: $\ln([D]/[C]) = -\Delta G^{\ddagger}/RT$

"In a chemical reaction that yields one product from one conformational isomer and a different product from another conformational isomer (and provided these two isomers are rapidly interconvertible relative to the rate of product formation, whereas the products do not interconvert), the product composition is not solely dependent on the relative proportions of the conformational isomers in the substrate; it is controlled by the difference in standard Gibbs energies of the respective transition states."

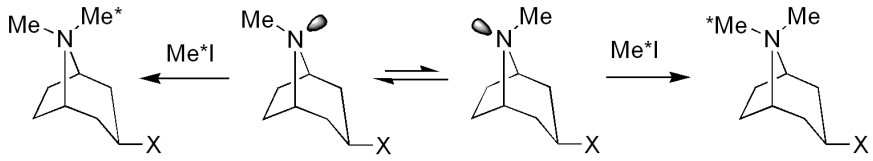
Gold, *Pure Appl. Chem.* **1979**, *51*, 1725-1801.

Attention:

- Product ratios are not to be interpreted as ground-state conformational equilibrium constants.

- Reaction outcome might be "contra-intuitive"

e. g. Methylation of the Tropanes:



X = Cl, OH minor product more stable less stable major product

J. Am. Chem. Soc. **1971**, *93*, 403;
J. Chem. Soc. **1962**, 3991.

see also: Cram-addition to α-chiral carbonyl functions

Review: *Chem. Rev.* **1983**, *83*, 84-134.